Supporting Information for:

Decomposition of A Key Intermediate In Ruthenium Catalyzed Olefin Metathesis Reactions

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General Considerations. Manipulation of organometallic compounds was performed using standard Schlenk techniques under an atmosphere of dry argon or in a nitrogen-filled Vacuum Atmospheres drybox (O_2 < 2 ppm). NMR spectra were recorded on a Varian Inova (499.85 MHz for ^{1}H; 202.34 MHz for ^{31}P; 125.69 MHz for ^{13}C) or on a Varian Mercury 300 (299.817 MHz for ^{1}H; 121.39 MHz for ^{31}P; 74.45 MHz for ^{13}C). ^{31}P NMR spectra were referenced using H_3PO_4 (= 0 ppm) as an external standard. Elemental analyses were performed at Desert Analytics (Tucson, AZ). Mass spectra were recorded on JEOL JMS 600H spectrophotometer. GC spectra were recorded on Hewlett-Packard 5970B MSD with 5890 GC.

Materials and Methods. Benzene, benzene-d_6, pentane, and methylene chloride were dried by passage through solvent purification columns.[1] CD_2Cl_2 was dried by vacuum transfer from CaH_2. All solvents are degassed by standard procedure. Allylbenzene was obtained from Aldrich and used as received. $(IMesH_2)(PCy_3)(Cl)_2Ru{=}CH_2$ was prepared according to literature procedure.[2]

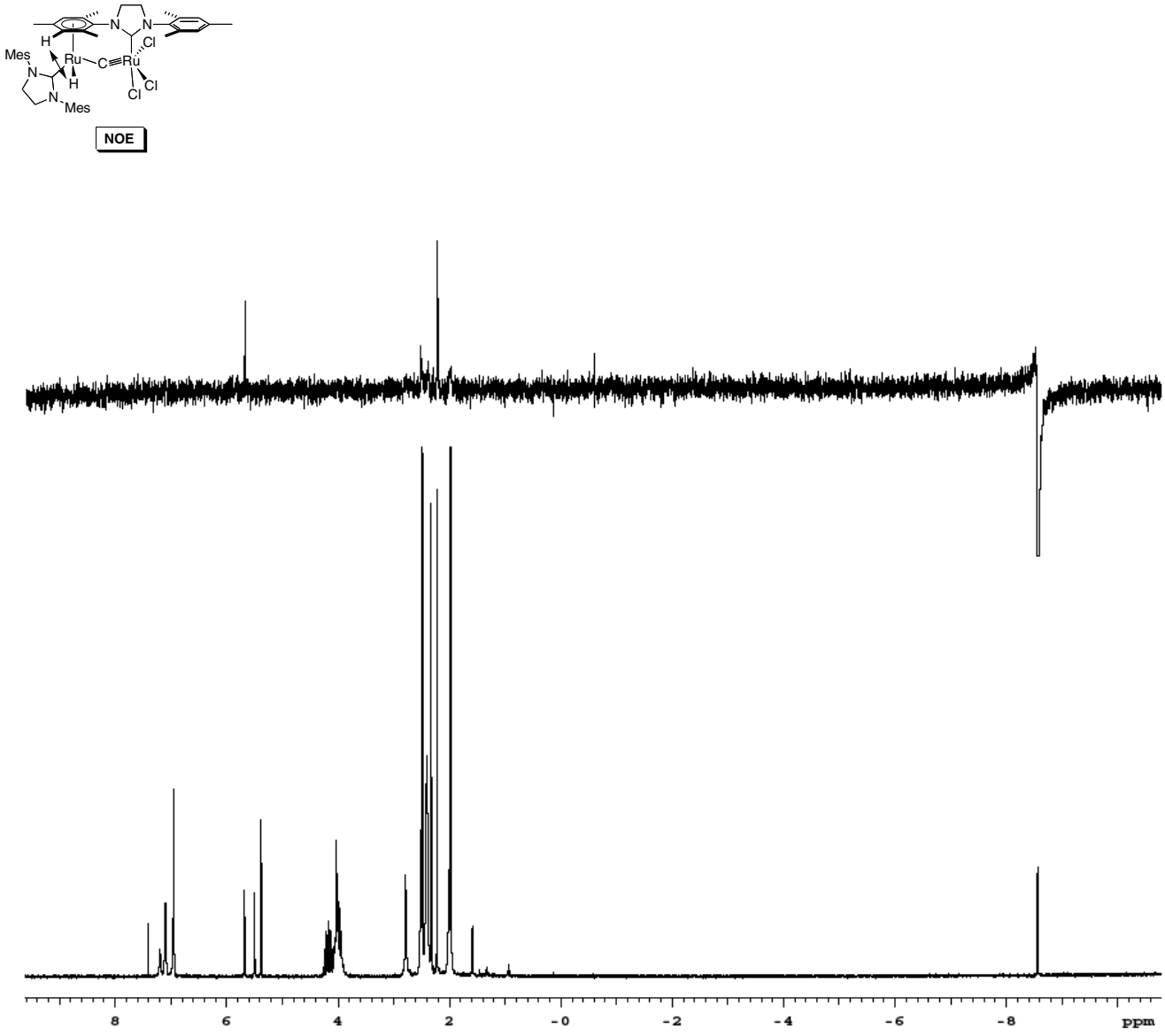
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996,** *15,* 1518-1520.
[2] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001,** *123,* 6543-6554.

Decomposition of complex 4. Complex **4** (48.3 mg, 0.06 mmol) was dissolved in benzene (2.7 mL) in a sealed tube. The reaction mixture was heated to 55 °C. Precipitation of orange-yellow crystalline solid was observed after 7 hrs. After 72 hrs, the precipitates were filtered, washed with benzene and dried under vacuum to afford complex **8** (13.2 mg, 46%). Methyltricyclohexylphosphonium chloride **9** was obtained along with some unidentified decomposed ruthenium species by the addition of pentane (5 mL) to the filtered benzene solution.

Dinuclear ruthenium complex 8. ^{1}H NMR (CD_2Cl_2): 7.14 (s, 1H), 7.05 (s. 1H), 7.04 (s, 1H), 6.90 (s, 3H), 5.62 (s, 1H), 5.44 (s, 1H), 4.19-4.06 (m, 2H), 3.99-3.86 (m, 6H), 2.73 (br s, 3H), 2.46 (br s, 3H), 2.45 (s, 3H), 2.43 (s, 3H), 2.4-2.3 (br, 9H), 2.27 (s, 3H), 2.17 (s, 3H), 1.96 (br s, 3H), 1.93 (s, 3H), 1.91 (s, 3H), -8.61 (s, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2): 413.98, 222.73, 207.87, 141.31, 140.11, 139.64, 139.04, 138.88, 138.86, 138.71, 138.44, 137.68, 135.13, 134.44, 133.65, 131.88, 130.60, 129.93, 129.89, 128.90, 128.68, 128.28, 120.30, 111.99, 111.85, 104.38, 100.60, 98.20, 51.63, 51.37, 48.81, 21.40, 20.99, 20.6-20.5 (br, m), 19.89, 19.25, 19.14, 18.53, 16.95. Anal. Calcd for $C_{43}H_{53}N_4Cl_3Ru_2$: C, 55.27; H, 5.72; N, 6.00. Found: C, 55.58; H, 5.64; N, 5.64. HRMS analysis (FAB) m/z: Calcd [M^+] 936.1424, found 936.1434.

Methyltricyclohexylphosphonium Chloride 9. ^{1}H NMR (C_6D_6): 2.61 (m, (CHC_5H_{10})$_3$-PCH_3^+, 3H), 2.42 (d, 3H, CH_3-PCy_3^+, J_{HP}= 12.6Hz), 1.85-1.00 (m, 30H). ^{13}C{^{1}H} NMR (C_6D_6): 30.43 (d, (CHC_5H_{10})$_3$-PCH_3^+, J_{CP}= 42.6Hz), 27.11 (d, J_{CP}= 3.1Hz), 26.47 (d, J_{CP} = 12.6 Hz), 25.86, 1.5 (d, CH_3-PCy_3^+, J_{CP}= 47.6Hz). ^{31}P{^{1}H} NMR (C_6D_6): 34.5 ppm. HRMS analysis (FAB) m/z: Calcd for $C_{19}H_{36}P$ [M^+]: 295.2555, found: 295.2557.

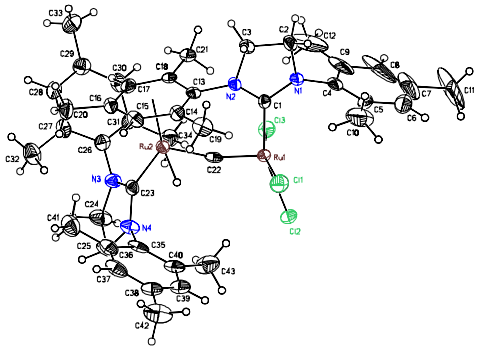
Figure S1. NOE and ^{1}H NMR spectra of **8**



Isomerization reaction of allylbenzene. Allylbenzene (17.1 mg, 0.15 mmol) and complex **8** (2.0mg, 1.5 mol %) were dissolved in CD_2Cl_2 (0.6 mL) in an NMR tube fitted with a screw cap. The resulting solution was heated to 40 °C and reaction was monitored by measuring the peak heights of allylic protons of allylbenzene and methyl protons of 1-phenyl-1-propene by ^1H NMR spectroscopy. After 1 day, yield of 1-phenyl-1-propene was determined by GC (76%, trans:cis = 8:1).

Crystal Structure Analysis of Complex 8

Contents



8

Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 223170.

Table S1. Crystal data and structure refinement for complex 8 (CCDC 223170).

Empirical formula	$C_{41}H_{53}Cl_3N_4Ru2 \cdot 1½(C_6H_6)$
Formula weight	1051.55
Crystallization Solvent	Benzene
Crystal Habit	Needle
Crystal size	0.38 x 0.07 x 0.04 mm^3
Crystal color	Yellow/orange

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 10984 reflections used in lattice determination	2.39 to 27.68°
Unit cell dimensions	a = 12.4536(9) Å b = 16.1001(11) Å β= 102.7980(10)° c = 24.7739(17) Å
Volume	4843.9(6) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1/c$
Density (calculated)	1.442 Mg/m^3
F(000)	2164
Data collection program	Bruker SMART v5.054
θ range for data collection	1.52 to 28.43°
Completeness to θ = 28.43°	92.5 %
Index ranges	$-15 \le h \le 16$, $-20 \le k \le 21$, $-32 \le l \le 32$
Data collection scan type	ω scans at 3 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	42525
Independent reflections	11284 [R_{int}= 0.0770]
Absorption coefficient	0.828 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9676 and 0.7437

Table S1 (cont.)

Structure solution and Refinement

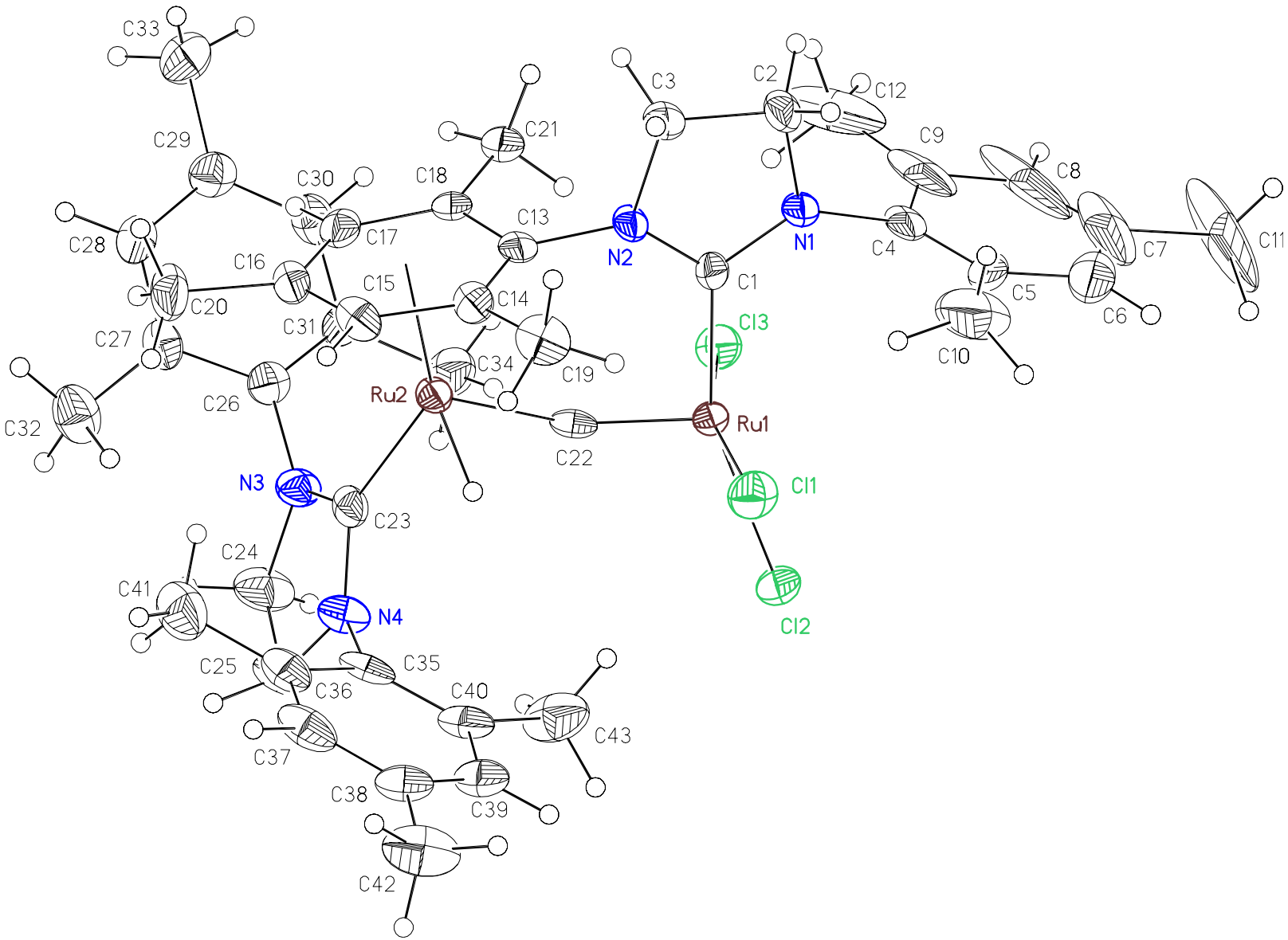
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Patterson method
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	11284 / 0 / 554
Treatment of hydrogen atoms	Mixed
Goodness-of-fit on F^2	1.396
Final R indices [$I>2\sigma(I)$, 7073 reflections]	R1 = 0.0488, *w*R2 = 0.0803
R indices (all data)	R1 = 0.0952, *w*R2 = 0.0859
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.005
Average shift/error	0.000
Largest diff. peak and hole	2.111 and -0.969 e.Å^{-3}

Special Refinement Details

All hydrogen atoms appear in the Fourier map and were refined as riding atoms with the exception of H2, a hydride on Ru2. This hydrogen was refined without restraints. However, care should be taken when interpreting the presence of this hydrogen based solely on the crystallographic data. Hydrides bound to metal atoms are notoriously difficult to resolve with x-ray diffraction data, therefore the results obtained here should be checked for consistency with data from other techniques. There is one residual peak in the final difference Fourier larger than 1e-/Å^3 and it is impossibly close to a solvent of crystallization.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.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C7
C11
C16
C15
C14
C1
C5
C6
C20
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C34
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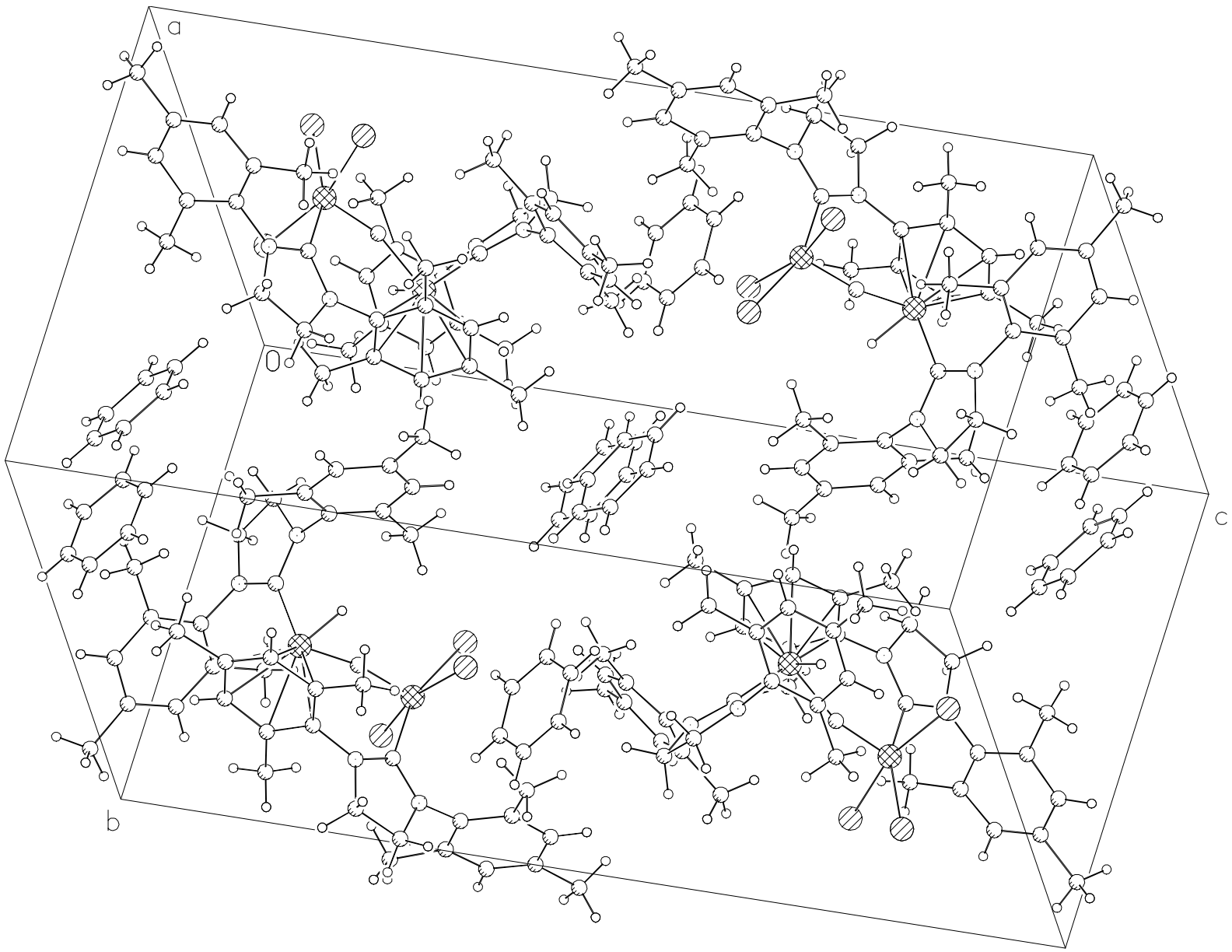
C39
C42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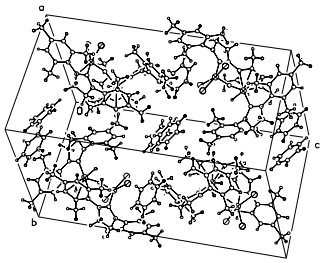
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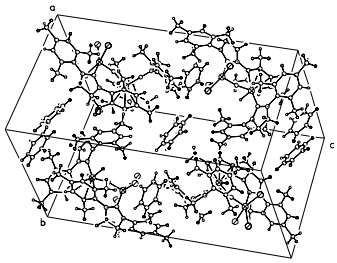
a
c
b

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 8 (CCDC 223170). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ru(1)	8847(1)	2335(1)	7123(1)	22(1)
Ru(2)	7130(1)	1878(1)	8038(1)	22(1)
Cl(1)	7366(1)	2136(1)	6352(1)	36(1)
Cl(2)	8966(1)	3735(1)	6794(1)	32(1)
Cl(3)	10589(1)	2596(1)	7711(1)	32(1)
N(1)	9591(3)	635(2)	6887(2)	28(1)
N(2)	8399(3)	537(2)	7400(1)	22(1)
N(3)	7501(3)	3233(2)	8932(1)	28(1)
N(4)	6234(3)	3588(2)	8219(2)	29(1)
C(1)	8985(3)	1078(2)	7160(2)	21(1)
C(2)	9455(4)	-272(2)	6934(2)	32(1)
C(3)	8621(4)	-345(2)	7291(2)	29(1)
C(4)	10388(5)	929(3)	6593(2)	48(2)
C(5)	10075(8)	1003(4)	6020(3)	86(3)
C(6)	10933(10)	1261(5)	5756(4)	141(6)
C(7)	12002(13)	1354(6)	6062(7)	178(9)
C(8)	12236(7)	1252(4)	6594(5)	137(5)
C(9)	11472(6)	1016(3)	6895(4)	71(2)
C(10)	8955(8)	827(4)	5699(3)	124(4)
C(11)	12919(11)	1624(4)	5757(6)	331(11)
C(12)	11786(5)	832(3)	7496(3)	88(2)
C(13)	7764(4)	686(2)	7796(2)	22(1)
C(14)	6605(4)	677(2)	7624(2)	26(1)
C(15)	5988(4)	772(2)	8038(2)	29(1)
C(16)	6496(4)	872(2)	8596(2)	29(1)
C(17)	7663(4)	889(2)	8749(2)	28(1)
C(18)	8318(3)	769(2)	8365(2)	23(1)
C(19)	6040(4)	542(3)	7032(2)	37(1)
C(20)	5817(4)	895(3)	9029(2)	43(1)
C(21)	9538(3)	739(2)	8524(2)	29(1)
C(22)	8059(3)	2296(2)	7601(2)	22(1)
C(23)	6927(3)	2975(2)	8434(2)	25(1)
C(24)	7289(4)	4117(3)	9048(2)	43(1)
C(25)	6299(4)	4315(3)	8586(2)	38(1)
C(26)	8193(4)	2733(3)	9345(2)	27(1)
C(27)	7739(4)	2402(3)	9769(2)	30(1)
C(28)	8395(4)	1866(3)	10149(2)	33(1)
C(29)	9455(4)	1663(3)	10110(2)	33(1)
C(30)	9898(4)	2058(3)	9714(2)	33(1)
C(31)	9289(4)	2613(3)	9333(2)	28(1)
C(32)	6613(4)	2634(3)	9840(2)	44(1)
C(33)	10096(4)	1024(3)	10491(2)	46(1)
C(34)	9802(4)	3053(3)	8919(2)	39(1)
C(35)	5311(3)	3526(2)	7756(2)	28(1)
C(36)	4318(4)	3213(3)	7844(2)	33(1)
C(37)	3419(4)	3203(3)	7402(2)	39(1)
C(38)	3472(4)	3497(3)	6884(2)	35(1)
C(39)	4458(4)	3788(3)	6812(2)	37(1)

C(40)	5392(4)	3817(2)	7237(2)	32(1)
C(41)	4222(4)	2881(3)	8390(2)	48(1)
C(42)	2457(4)	3525(3)	6422(2)	57(2)
C(43)	6462(4)	4128(3)	7126(2)	53(2)
C(51)	3888(5)	861(4)	9939(3)	68(2)
C(52)	3294(5)	309(4)	9557(3)	75(2)
C(53)	2542(4)	603(4)	9101(3)	63(2)
C(54)	2400(4)	1455(4)	9034(2)	59(2)
C(55)	2972(4)	1979(4)	9418(2)	54(2)
C(56)	3719(5)	1682(4)	9876(3)	60(2)
C(61)	4649(7)	4204(4)	-47(4)	77(2)
C(62)	5441(7)	4419(4)	389(3)	69(2)
C(63)	5818(5)	5224(6)	439(3)	86(2)

Table S3. Selected bond lengths [Å] and angles [°] for complex 8 (CCDC 223170).

Ru(1)-C(22)	1.698(4)	C(22)-Ru(1)-C(1)	89.29(17)
Ru(1)-C(1)	2.031(4)	C(22)-Ru(1)-Cl(1)	95.19(13)
Ru(1)-Cl(1)	2.3653(12)	C(1)-Ru(1)-Cl(1)	86.80(12)
Ru(1)-Cl(3)	2.3669(11)	C(22)-Ru(1)-Cl(3)	99.79(13)
Ru(1)-Cl(2)	2.4124(11)	C(1)-Ru(1)-Cl(3)	95.29(12)
Ru(2)-H(2)	1.45(3)	Cl(1)-Ru(1)-Cl(3)	164.89(4)
Ru(2)-C(22)	1.875(4)	C(22)-Ru(1)-Cl(2)	110.97(13)
Ru(2)-C(23)	2.063(4)	C(1)-Ru(1)-Cl(2)	159.29(12)
		Cl(1)-Ru(1)-Cl(2)	87.09(4)
		Cl(3)-Ru(1)-Cl(2)	85.74(4)
		H(2)-Ru(2)-C(22)	74.1(13)
		H(2)-Ru(2)-C(23)	83.9(13)
		C(22)-Ru(2)-C(23)	97.12(16)
		Ru(1)-C(22)-Ru(2)	160.3(2)

Table S4. Bond lengths [Å] and angles [°] for complex 8 (CCDC 223170).

Ru(1)-C(22)	1.698(4)	C(29)-C(30)	1.382(6)
Ru(1)-C(1)	2.031(4)	C(29)-C(33)	1.501(6)
Ru(1)-Cl(1)	2.3653(12)	C(30)-C(31)	1.396(6)
Ru(1)-Cl(3)	2.3669(11)	C(31)-C(34)	1.502(6)
Ru(1)-Cl(2)	2.4124(11)	C(35)-C(40)	1.394(6)
Ru(2)-H(2)	1.45(3)	C(35)-C(36)	1.396(6)
Ru(2)-C(22)	1.875(4)	C(36)-C(37)	1.382(6)
Ru(2)-C(23)	2.063(4)	C(36)-C(41)	1.483(6)
Ru(2)-C(13)	2.207(4)	C(37)-C(38)	1.384(6)
Ru(2)-C(14)	2.219(4)	C(38)-C(39)	1.362(6)
Ru(2)-C(15)	2.280(4)	C(38)-C(42)	1.506(6)
Ru(2)-C(18)	2.345(4)	C(39)-C(40)	1.385(6)
Ru(2)-C(17)	2.357(4)	C(40)-C(43)	1.503(6)
Ru(2)-C(16)	2.375(4)	C(51)-C(56)	1.343(7)
N(1)-C(1)	1.328(5)	C(51)-C(52)	1.387(8)
N(1)-C(4)	1.435(6)	C(52)-C(53)	1.382(8)
N(1)-C(2)	1.478(5)	C(53)-C(54)	1.389(7)
N(2)-C(1)	1.357(5)	C(54)-C(55)	1.351(7)
N(2)-C(13)	1.411(5)	C(55)-C(56)	1.382(7)
N(2)-C(3)	1.483(5)	C(61)-C(62)	1.337(8)
N(3)-C(23)	1.346(5)	C(61)-C(63)#1	1.371(8)
N(3)-C(26)	1.432(5)	C(62)-C(63)	1.376(8)
N(3)-C(24)	1.487(5)	C(63)-C(61)#1	1.371(8)
N(4)-C(23)	1.341(5)		
N(4)-C(35)	1.437(5)	C(22)-Ru(1)-C(1)	89.29(17)
N(4)-C(25)	1.472(5)	C(22)-Ru(1)-Cl(1)	95.19(13)
C(2)-C(3)	1.510(5)	C(1)-Ru(1)-Cl(1)	86.80(12)
C(4)-C(5)	1.391(8)	C(22)-Ru(1)-Cl(3)	99.79(13)
C(4)-C(9)	1.398(8)	C(1)-Ru(1)-Cl(3)	95.29(12)
C(5)-C(6)	1.434(11)	Cl(1)-Ru(1)-Cl(3)	164.89(4)
C(5)-C(10)	1.473(10)	C(22)-Ru(1)-Cl(2)	110.97(13)
C(6)-C(7)	1.386(19)	C(1)-Ru(1)-Cl(2)	159.29(12)
C(7)-C(8)	1.296(17)	Cl(1)-Ru(1)-Cl(2)	87.09(4)
C(7)-C(11)	1.565(12)	Cl(3)-Ru(1)-Cl(2)	85.74(4)
C(8)-C(9)	1.385(9)	H(2)-Ru(2)-C(22)	74.1(13)
C(9)-C(12)	1.484(9)	H(2)-Ru(2)-C(23)	83.9(13)
C(13)-C(14)	1.411(6)	C(22)-Ru(2)-C(23)	97.12(16)
C(13)-C(18)	1.430(6)	H(2)-Ru(2)-C(13)	110.6(13)
C(14)-C(15)	1.420(6)	C(22)-Ru(2)-C(13)	81.52(16)
C(14)-C(19)	1.496(6)	C(23)-Ru(2)-C(13)	164.18(17)
C(15)-C(16)	1.394(6)	H(2)-Ru(2)-C(14)	86.6(13)
C(16)-C(17)	1.419(6)	C(22)-Ru(2)-C(14)	101.67(16)
C(16)-C(20)	1.506(6)	C(23)-Ru(2)-C(14)	155.68(16)
C(17)-C(18)	1.396(5)	C(13)-Ru(2)-C(14)	37.19(15)
C(18)-C(21)	1.484(5)	H(2)-Ru(2)-C(15)	93.9(13)
C(24)-C(25)	1.520(6)	C(22)-Ru(2)-C(15)	138.18(16)
C(26)-C(31)	1.385(5)	C(23)-Ru(2)-C(15)	121.74(15)
C(26)-C(27)	1.402(6)	C(13)-Ru(2)-C(15)	65.25(15)
C(27)-C(28)	1.400(6)	C(14)-Ru(2)-C(15)	36.78(14)
C(27)-C(32)	1.499(6)	H(2)-Ru(2)-C(18)	147.0(13)
C(28)-C(29)	1.384(6)	C(22)-Ru(2)-C(18)	92.88(15)

C(23)-Ru(2)-C(18)	128.46(16)	N(2)-C(13)-Ru(2)	128.7(3)
C(13)-Ru(2)-C(18)	36.47(14)	C(18)-C(13)-Ru(2)	77.0(2)
C(14)-Ru(2)-C(18)	66.10(15)	C(13)-C(14)-C(15)	117.4(4)
C(15)-Ru(2)-C(18)	75.57(15)	C(13)-C(14)-C(19)	121.7(4)
H(2)-Ru(2)-C(17)	156.6(13)	C(15)-C(14)-C(19)	120.8(4)
C(22)-Ru(2)-C(17)	124.48(16)	C(13)-C(14)-Ru(2)	71.0(2)
C(23)-Ru(2)-C(17)	105.47(16)	C(15)-C(14)-Ru(2)	73.9(2)
C(13)-Ru(2)-C(17)	63.70(15)	C(19)-C(14)-Ru(2)	127.3(3)
C(14)-Ru(2)-C(17)	76.23(15)	C(16)-C(15)-C(14)	121.9(4)
C(15)-Ru(2)-C(17)	62.89(16)	C(16)-C(15)-Ru(2)	76.3(2)
C(18)-Ru(2)-C(17)	34.55(13)	C(14)-C(15)-Ru(2)	69.3(2)
H(2)-Ru(2)-C(16)	122.8(13)	C(15)-C(16)-C(17)	118.7(4)
C(22)-Ru(2)-C(16)	155.20(16)	C(15)-C(16)-C(20)	120.4(4)
C(23)-Ru(2)-C(16)	102.43(15)	C(17)-C(16)-C(20)	120.8(4)
C(13)-Ru(2)-C(16)	75.50(15)	C(15)-C(16)-Ru(2)	68.9(2)
C(14)-Ru(2)-C(16)	64.68(15)	C(17)-C(16)-Ru(2)	71.9(2)
C(15)-Ru(2)-C(16)	34.78(14)	C(20)-C(16)-Ru(2)	135.2(3)
C(18)-Ru(2)-C(16)	62.97(15)	C(18)-C(17)-C(16)	122.3(4)
C(17)-Ru(2)-C(16)	34.89(14)	C(18)-C(17)-Ru(2)	72.2(2)
C(1)-N(1)-C(4)	128.1(3)	C(16)-C(17)-Ru(2)	73.2(2)
C(1)-N(1)-C(2)	113.8(3)	C(17)-C(18)-C(13)	117.1(4)
C(4)-N(1)-C(2)	118.0(3)	C(17)-C(18)-C(21)	122.8(4)
C(1)-N(2)-C(13)	129.4(3)	C(13)-C(18)-C(21)	120.0(4)
C(1)-N(2)-C(3)	113.2(3)	C(17)-C(18)-Ru(2)	73.2(2)
C(13)-N(2)-C(3)	116.6(3)	C(13)-C(18)-Ru(2)	66.5(2)
C(23)-N(3)-C(26)	126.5(3)	C(21)-C(18)-Ru(2)	130.4(3)
C(23)-N(3)-C(24)	113.1(3)	Ru(1)-C(22)-Ru(2)	160.3(2)
C(26)-N(3)-C(24)	120.2(3)	N(4)-C(23)-N(3)	107.5(4)
C(23)-N(4)-C(35)	126.6(3)	N(4)-C(23)-Ru(2)	125.3(3)
C(23)-N(4)-C(25)	113.5(3)	N(3)-C(23)-Ru(2)	127.1(3)
C(35)-N(4)-C(25)	118.2(3)	N(3)-C(24)-C(25)	101.7(3)
N(1)-C(1)-N(2)	107.4(3)	N(4)-C(25)-C(24)	102.8(3)
N(1)-C(1)-Ru(1)	124.4(3)	C(31)-C(26)-C(27)	121.7(4)
N(2)-C(1)-Ru(1)	127.8(3)	C(31)-C(26)-N(3)	120.2(4)
N(1)-C(2)-C(3)	103.2(3)	C(27)-C(26)-N(3)	118.1(4)
N(2)-C(3)-C(2)	102.3(3)	C(28)-C(27)-C(26)	117.8(4)
C(5)-C(4)-C(9)	123.8(6)	C(28)-C(27)-C(32)	119.7(4)
C(5)-C(4)-N(1)	118.5(6)	C(26)-C(27)-C(32)	122.4(4)
C(9)-C(4)-N(1)	117.2(5)	C(29)-C(28)-C(27)	121.4(4)
C(4)-C(5)-C(6)	115.0(9)	C(30)-C(29)-C(28)	118.5(4)
C(4)-C(5)-C(10)	123.5(6)	C(30)-C(29)-C(33)	121.5(4)
C(6)-C(5)-C(10)	121.5(8)	C(28)-C(29)-C(33)	120.0(4)
C(7)-C(6)-C(5)	120.2(11)	C(29)-C(30)-C(31)	122.1(4)
C(8)-C(7)-C(6)	121.0(11)	C(26)-C(31)-C(30)	117.7(4)
C(8)-C(7)-C(11)	120.2(16)	C(26)-C(31)-C(34)	121.3(4)
C(6)-C(7)-C(11)	118.7(14)	C(30)-C(31)-C(34)	120.9(4)
C(7)-C(8)-C(9)	123.7(12)	C(40)-C(35)-C(36)	120.9(4)
C(8)-C(9)-C(4)	115.9(8)	C(40)-C(35)-N(4)	120.3(4)
C(8)-C(9)-C(12)	122.4(8)	C(36)-C(35)-N(4)	118.6(4)
C(4)-C(9)-C(12)	121.7(5)	C(37)-C(36)-C(35)	118.0(5)
C(14)-C(13)-N(2)	118.7(4)	C(37)-C(36)-C(41)	120.2(4)
C(14)-C(13)-C(18)	122.5(4)	C(35)-C(36)-C(41)	121.7(4)
N(2)-C(13)-C(18)	118.6(4)	C(38)-C(37)-C(36)	122.3(4)
C(14)-C(13)-Ru(2)	71.8(2)	C(39)-C(38)-C(37)	117.9(4)

C(39)-C(38)-C(42)	121.3(5)	C(52)-C(53)-C(54)	118.7(6)
C(37)-C(38)-C(42)	120.7(5)	C(55)-C(54)-C(53)	120.0(6)
C(38)-C(39)-C(40)	122.9(5)	C(54)-C(55)-C(56)	121.1(6)
C(39)-C(40)-C(35)	117.9(4)	C(51)-C(56)-C(55)	119.7(6)
C(39)-C(40)-C(43)	120.2(5)	C(62)-C(61)-C(63)#1	121.3(6)
C(35)-C(40)-C(43)	121.9(4)	C(61)-C(62)-C(63)	119.6(6)
C(56)-C(51)-C(52)	120.3(6)	C(62)-C(63)-C(61)#1	119.1(6)
C(53)-C(52)-C(51)	120.1(6)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Table S5. Anisotropic displacement parameters ($Å^2 x 10^4$) for complex 8 (CCDC 223170). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	257(2)	162(2)	251(2)	26(2)	99(2)	14(2)
Ru(2)	232(2)	168(2)	283(2)	3(2)	104(2)	-7(2)
Cl(1)	428(7)	360(7)	269(7)	-25(5)	14(5)	10(5)
Cl(2)	436(7)	191(6)	378(7)	60(5)	164(6)	7(5)
Cl(3)	248(6)	314(6)	402(7)	57(5)	91(5)	-23(5)
N(1)	370(20)	165(19)	350(20)	47(17)	195(19)	58(17)
N(2)	280(20)	132(18)	280(20)	-26(16)	136(17)	-6(16)
N(3)	350(20)	210(20)	270(20)	-36(17)	45(18)	38(17)
N(4)	250(20)	220(20)	360(20)	-42(18)	-14(18)	22(17)
C(1)	260(30)	220(20)	180(20)	-12(19)	69(19)	11(19)
C(2)	430(30)	200(20)	390(30)	-20(20)	240(20)	20(20)
C(3)	390(30)	150(20)	370(30)	-10(20)	170(20)	10(20)
C(4)	720(40)	130(30)	780(40)	170(30)	570(40)	180(30)
C(5)	1720(80)	420(40)	770(50)	380(40)	940(60)	620(50)
C(6)	2940(150)	510(50)	1350(90)	560(50)	1700(110)	950(90)
C(7)	2960(170)	290(50)	3100(200)	510(80)	2770(180)	600(90)
C(8)	1060(70)	160(40)	3430(160)	-90(60)	1650(100)	10(40)
C(9)	640(50)	90(30)	1640(70)	40(40)	730(50)	80(30)
C(10)	2250(110)	1160(60)	330(40)	100(40)	300(50)	1210(70)
C(11)	5100(200)	460(50)	6400(200)	740(90)	5600(200)	590(80)
C(12)	420(40)	360(40)	1690(80)	-100(40)	-100(40)	120(30)
C(13)	300(30)	70(20)	310(30)	-7(18)	110(20)	2(18)
C(14)	250(30)	200(20)	360(30)	-10(20)	120(20)	-62(19)
C(15)	220(30)	200(20)	500(30)	-50(20)	150(20)	-76(19)
C(16)	380(30)	140(20)	410(30)	-20(20)	240(20)	-60(20)
C(17)	400(30)	180(20)	270(30)	12(19)	120(20)	-10(20)
C(18)	310(30)	110(20)	280(30)	41(18)	90(20)	41(19)
C(19)	290(30)	320(30)	460(30)	-70(20)	20(20)	-90(20)
C(20)	590(40)	340(30)	480(30)	-30(20)	360(30)	-90(30)
C(21)	370(30)	200(20)	320(30)	30(20)	110(20)	60(20)
C(22)	220(20)	100(20)	310(30)	-22(19)	-6(19)	13(18)
C(23)	230(20)	230(20)	310(30)	0(20)	130(20)	-31(19)
C(24)	550(40)	260(30)	430(30)	-110(20)	10(30)	70(20)
C(25)	300(30)	260(30)	530(30)	-110(20)	-10(20)	70(20)
C(26)	310(30)	260(20)	210(20)	-50(20)	20(20)	-20(20)
C(27)	290(30)	320(30)	310(30)	-70(20)	110(20)	-40(20)
C(28)	370(30)	370(30)	280(30)	20(20)	110(20)	-20(20)
C(29)	340(30)	350(30)	270(30)	-10(20)	10(20)	10(20)
C(30)	260(30)	440(30)	310(30)	-40(20)	60(20)	0(20)
C(31)	330(30)	270(30)	250(30)	30(20)	70(20)	-30(20)
C(32)	320(30)	590(30)	400(30)	-90(30)	90(20)	0(30)
C(33)	500(40)	540(30)	310(30)	90(30)	50(30)	70(30)
C(34)	340(30)	390(30)	460(30)	80(20)	110(20)	-50(20)
C(35)	180(30)	150(20)	470(30)	-90(20)	-20(20)	47(19)
C(36)	280(30)	250(30)	460(30)	-100(20)	90(20)	10(20)
C(37)	190(30)	300(30)	680(40)	-120(30)	80(30)	-10(20)
C(38)	350(30)	190(20)	460(30)	0(20)	-10(20)	20(20)

C(39)	420(30)	220(30)	470(30)	50(20)	70(30)	50(20)
C(40)	230(30)	170(20)	530(30)	40(20)	30(20)	30(20)
C(41)	400(30)	510(40)	570(40)	-40(30)	200(30)	-20(30)
C(42)	500(40)	370(30)	700(40)	-140(30)	-140(30)	10(30)
C(43)	340(30)	460(30)	780(40)	240(30)	80(30)	-40(30)
C(51)	560(40)	860(50)	590(40)	290(40)	60(30)	-40(40)
C(52)	550(40)	620(40)	1130(60)	370(40)	280(40)	30(40)
C(53)	340(40)	800(50)	740(50)	60(40)	110(30)	-90(30)
C(54)	320(30)	770(50)	630(40)	200(40)	50(30)	-40(30)
C(55)	340(30)	550(40)	750(50)	40(30)	160(30)	-50(30)
C(56)	490(40)	770(50)	600(40)	10(40)	250(30)	10(30)
C(61)	910(60)	570(50)	900(60)	70(50)	340(50)	30(40)
C(62)	1100(60)	600(50)	460(40)	80(30)	340(40)	390(40)
C(63)	560(50)	1170(70)	810(60)	-340(50)	90(40)	250(50)